Processing and adsorption control in ZnO single nanowire photodetectors

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Abstract— **ZnO single nanowire photodetectors have been measured in different ambient conditions in order to understand and control adsorption processes on the surface. A decrease in the conductivity has been observed as a function of time when the nanowires are exposed to air, due to adsorbed O_2/H_2O species at the nanowire surface. In order to have a device with stable characteristics in time, thermal desorption has been used to recover the original conductivity followed by PMMA coating of the exposed nanowire surface.**

Keywords-ZnO; nanowires; adsorption; nanophotodetectors; transport.

I. INTRODUCTION

ZnO-based nanowires are being intensively researched because they have a combination of attractive mechanical, optical and magnetic properties. Due its direct wide bandgap (3.37 eV), high exciton binding energy (60 meV) and the fact that it can be easily be grown in one dimensional structures, ZnO is a promising material for nanophotodetectors in the UV range [1]. However, the main problem to obtain a stable single ZnO nanodevice is the surface adsorption. O_2 and H_2O molecules are adsorbed on the surface increasing the depletion region which reduces substantially the conductivity of a single nanowire. This makes the response of the device not reproducible.

In order to understand and control the depletion region of single ZnO nanowires we have developed a method to reduce the impact of adsorption process covering the surface with a commercial Poly(methyl methacrylate) (PMMA) resist after a thermal cycle. We have demonstrated that the adsorption rate increases substantially when the nanowire is electrically polarized, therefore studies of this effect have been done in order to obtain a stable photodetector with high responsivity in the UV range [2].

II. EXPERIMENTAL DETAIL

ZnO nanowires were grown on a-plane sapphire substrates by RPE-MOCVD and show a bandgap of 3.3 eV as measured by PL. The growth temperature was 300 ºC. Nanowires are 100–200 nm in diameter and 2-5 µm in length. In order to electrically connect single nanowires, they were first dispersed by sonication in isopropanol and deposited onto a 70 nm-thick SiO_2/Si substrate. Electrode patterns were defined by electron-beam lithography followed by electron-beam evaporation of Ti(10 nm)/Au(80 nm) electrodes on a ZnO single nanowire followed by a lift-off process. The contacts were annealed at 550ºC for 1 minute under a nitrogen ambient leading to a highly ohmic behaviour. In selected devices commercial PMMA resist was deposited after thermal annealing to reduce the adsorption on surface. A scanning electron microscopy (SEM) image of a single nanowire electrically connected can be seen in the inset of Figure 1.

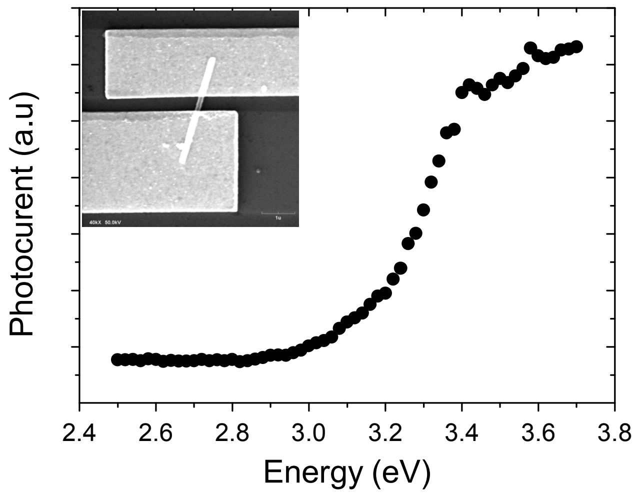

Figure 1. Light absorption spectrum of a single ZnO nanowire at 0.2 V. The inset shows a SEM image of a single nanowire photodetector.

III. RESULTS AND DISCUSSION

Photocurrent measurements on single nanowire photodetectors have been performed in air conditions, showing high responsivity to UV illumination above band gap energy (Fig.1). The I-V curves in the dark and above bandgap illumination are shown in figure 2. A current increase of more than one order of magnitude is obtained under illumination.

However, in air conditions gas adsorption processes occur on the ZnO surface. Oxygen molecules are adsorbed on the nanowire surface and capture the free electrons present in the oxide semiconductor, [$O_2(g) + e^- \rightarrow O_2^-(ad)$]. A depletion region near the surface is formed reducing the conductance of the single nanowire. When illuminating with a photon energy above E_g, electron-hole pairs are generated and holes migrate to the surface and recombine with the electrons trapped on the surface, and consequently oxygen is photodesorbed [$h^+ + O_2^-(ad) \rightarrow O_2(g)$][3].

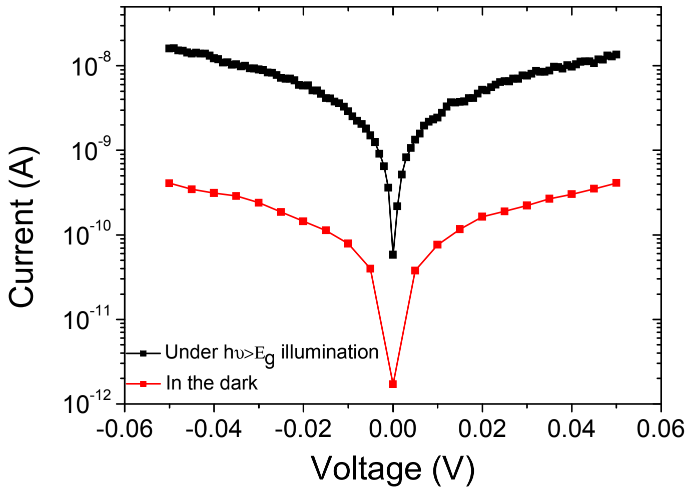

Figure 2. IV characteristics in the dark and under illumination for a single ZnO nanowire.

This process makes the electrical characteristcs of single ZnO nanowires and its response to illumination highly not reproducible. It is thus a really important problem which needs to be solved if we want to fabricate ZnO nanodevices with reliable characteristics on time.

A. Adsorption dynamics

In order to understand the adsorption processes on the surface we have measured the current decay with time of a single nanowire in the dark under different conditions at 1V. In air conditions we have observed a strong reduction of the conductance due to adsorption of O_2 and H_2O molecules. On the other hand, in vacuum conditions we do not observe this degradation (Fig.3). This shows the high sensitivity of the nanowire electrical conductance to the gas species being adsorbed at the surface [4,5].

To reduce the adsorption processes on the surface we have covered the nanowire surface with commercial PMMA resist after an annealing process in nitrogen ambient. With this passivation layer we have minimized gas adsorption at the surface. Nanowires covered with PMMA measured in the same ambient conditions in a period of time of 120 hours presents much lower sensitivity to air exposure than those not passivated (Fig.4)[6,7].

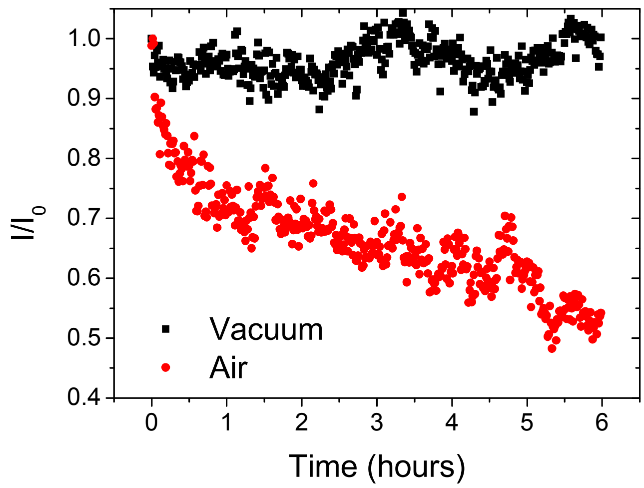

Figure 3. Relative current decay versus time of an uncoated single nanowire under vacuum and air conditions at 1V.

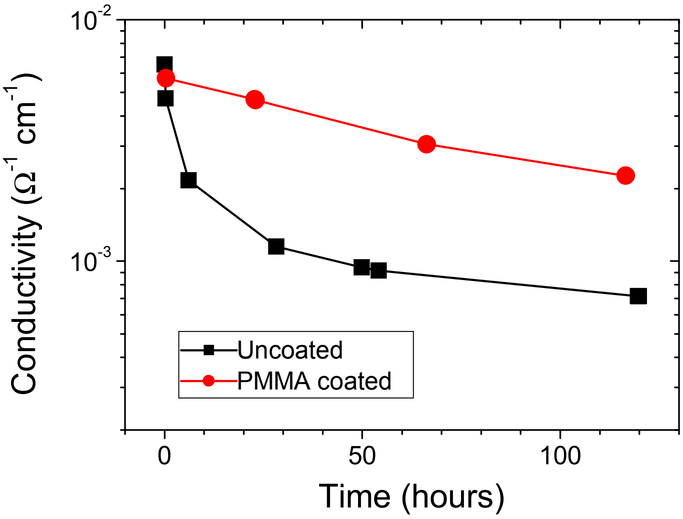

Figure 4. Time decay of a single nanowire conductivity exposed to air.

B. Adsorption control

To develop a ZnO-based single nanowire photodetector we have to control first adsorption processes on the surface as we have seen. Two methods could be use to remove adsorbents on the surface: Thermal desorption and UV photodesorption. In this paper we we focus on the analysis of thermal desorption.

Under vacuum conditions, exposing the nanowire to higher temperatures leads to higher conductivities. This is because when we increase temperature we are promoting desorption, decreasing the depletion region and increasing the nanowire conductance. We have analyzed the effect of the annealing temperature in order to know the critical temperature at which desorption processes on the nanowire start. After the annealing process we have measured the I-V curves again at room temperature (Fig.5).

After the first measurement in air conditions we have exposed the nanowire to a vacuum environment. No significative change in conductivity has been observed. Once in vacuum, we have annealed the sample 20 minutes with different temperatures. A slow increase of conductivity has been observed with annealing temperatures below 450 K. However, we observed a very large change in conductivity when increasing annealing temperature above 450 K (Table I). This means that desorption processes became significant above 450 K. At 500 K, a increase in conductivity of one order of magnitude is observed after annealing.

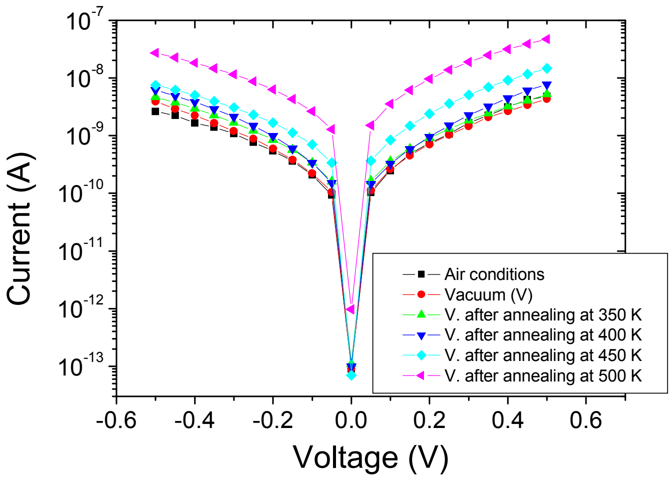

Figure 5. IV characteristics in dark conditions after different annealing temperatures. Measurement temperature is 297 K.

TABLE I. CONDUCTIVITY AFTER DIFFERENT ANNEALING TEMPERATURES.

Measurements conditions	Conductivity improvement	
	Conductivity (Ω^{-1} *cm^{-1} *10^{-3})	Improvement of conductivity (%)
Air conditons	1.34	-
Vacuum	1.38	3.9
Vacuum after annealing at 350 K	1.72	29.3
Vacuum after annealing at 400 K	2.32	75.2
Vacuum after annealing at 450 K	3.94	198.3
Vacuum after annealing at 500 K	13.8	947.1

IV. CONCLUSIONS

Under air conditions ZnO-based single nanowire photodetectors show high responsivity to UV illumination. However, this conductivity depends on gas adsorption at the surface, most likely O_2 and H_2O. To reduce adsorption processes we have annealed the sample followed by PMMA pasivattion. Under these controlled surface conditions, the ZnO-based nanowire photodetector can have a high and reproducible responsivity in air.

We have demonstrated that in a vacuum environment it is possible to remove adsorbents from the surface annealing the samples. An increase of conductivity by about 1 order of magnitude has been measured after annealing at 500 K.

V. ACKNOWLEDGMENT

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